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PHYSICAL-CHEMICAL EXAMINATION OF THE  $N_2O_3-SO_3-H_2O$  SYSTEM

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16. Abstract When $(\text{NO})\text{HSO}_4$ is added to absolute $\text{H}_2\text{SO}_4$ , specific conduc- tivity rises sharply, possibly due to an increase in mutual interionic effects and viscosity as the $(\text{NO})\text{HSO}_4$ concentra- tion rises. The addition of $\text{SO}_3$ to the solution yields a precipitate; a combination of analysis, IR spectroscopy and x-ray diffraction techniques indicates that this precipitate is $(\text{NO})\text{HS}_2\text{O}_7$ .			
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# PHYSICAL-CHEMICAL EXAMINATION OF THE $\text{N}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ SYSTEM

C. Linström and G. Malyska

Hantsch's determinations of the molar mass of  $(\text{NO})\text{HSO}_4$  /345\* in absolute sulfuric acid [1] yielded a mean value of 71.4 for four values varying from 70.8 to 72.5; whereas the calculated value was 127.076. Thus  $(\text{NO})\text{HSO}_4$  is highly dissociated in absolute  $\text{H}_2\text{SO}_4$ .

It was therefore of interest to investigate how the addition of  $(\text{NO})\text{HSO}_4$  to absolute  $\text{H}_2\text{SO}_4$  affects the specific conductivity of anhydrous sulfuric acid. It develops that at first, specific conductivity rises sharply as the solution's  $(\text{NO})\text{HSO}_4$  content increases (Fig. 1). Each of the three isotherms demon-

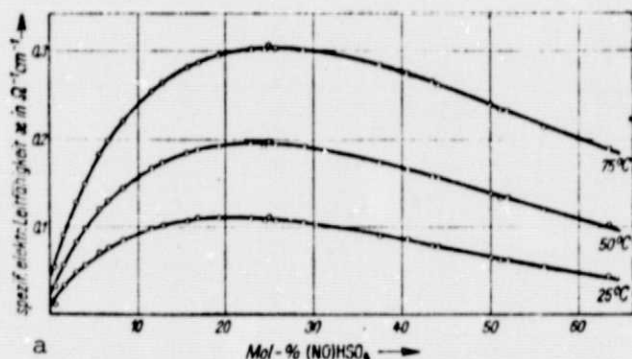


Fig. 1. Specific electrical conductivity for solutions of  $(\text{NO})\text{HSO}_4$  in anhydrous  $\text{H}_2\text{SO}_4$ .

Key: a. Specific conductivity  $\kappa$  in  $\Omega^{-1}\text{cm}^{-1}$ .

et al. [3] for solutions of alkaline and alkaline earth hydrogen sulfates in absolute  $\text{H}_2\text{SO}_4$ . Gube [4], who examined the viscosity

strates a maximum, the position of which is displaced as a function of temperature from  $\kappa = 0.1100 \Omega^{-1}\text{cm}^{-1}$  at 25 °C and 21.8 Mol%  $(\text{NO})\text{HSO}_4$  to  $\kappa = 0.340 \Omega^{-1}\text{cm}^{-1}$  at 75 °C and 25.5 Mol%  $(\text{NO})\text{HSO}_4$ .

The initial rise in the isotherms corresponds to the conductivity isotherm curves obtained by Gillespie and Wasif [2] and Bass, Flowers

\* Numbers in the margin indicate pagination in the foreign text.

of solutions of  $(\text{NO})\text{HSO}_4$  in absolute  $\text{H}_2\text{SO}_4$ , found a sharp rise after 20 Mol%  $(\text{NO})\text{HSO}_4$  at 25 °C, the start of which shifted in the direction of higher concentrations of  $(\text{NO})\text{HSO}_4$  as the concentration rose. Thus, in addition to the increase in inter-ionic mutual effects as the  $(\text{NO})\text{HSO}_4$  concentration increases, the sharp increase in viscosity may also be responsible for the decrease in specific conductivity.

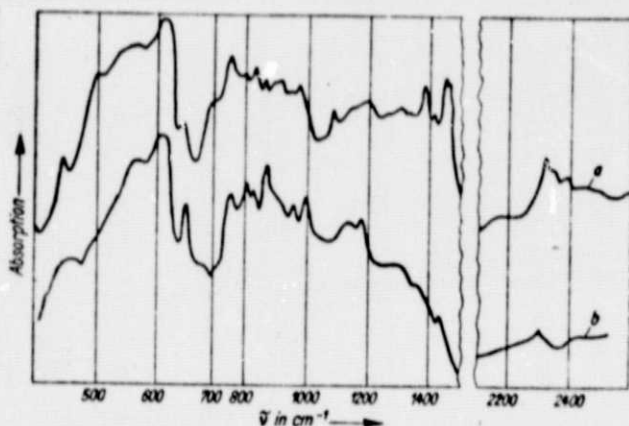


Fig. 2. Infrared spectrum of  $(\text{NO})\text{HS}_2\text{O}_7$ : a = sample in Nujol; b = sample in hexachlorobutadiene

The specific conductivity of solutions of  $(\text{NO})\text{HSO}_4$  in absolute  $\text{H}_2\text{SO}_4$  is also decreased by the addition of  $\text{SO}_3$ . A subsequent paper will report on these results.

When  $\text{SO}_3$  is introduced into a solution of  $(\text{NO})\text{HSO}_4$ , a crystalline solid phase is

precipitated. This precipitate was cleared of the mother liquor on clay over  $\text{P}_4\text{O}_{10}$  in a desiccator, and then examined by element analysis, IR spectroscopy and x-rays.

The analysis yielded 0.0177 Mol sulfur and 0.0088 Mol nitrogen, or 0.0195 Mol sulfur and 0.0096 Mol nitrogen, respectively. This corresponds to a sulfur-nitrogen molar ratio of 2:1 or 2.05:1.

For IR spectroscopy, the substance was incorporated in Nujol and examined between Si plates in the wave number range 400–2500  $\text{cm}^{-1}$ . Since Nujol demonstrates its own absorption in the range around 750  $\text{cm}^{-1}$ , the substance was also incorporated in hexachlorobutadiene and examined in the same wave number range. The readings are given in Fig. 2. A comparison of our results

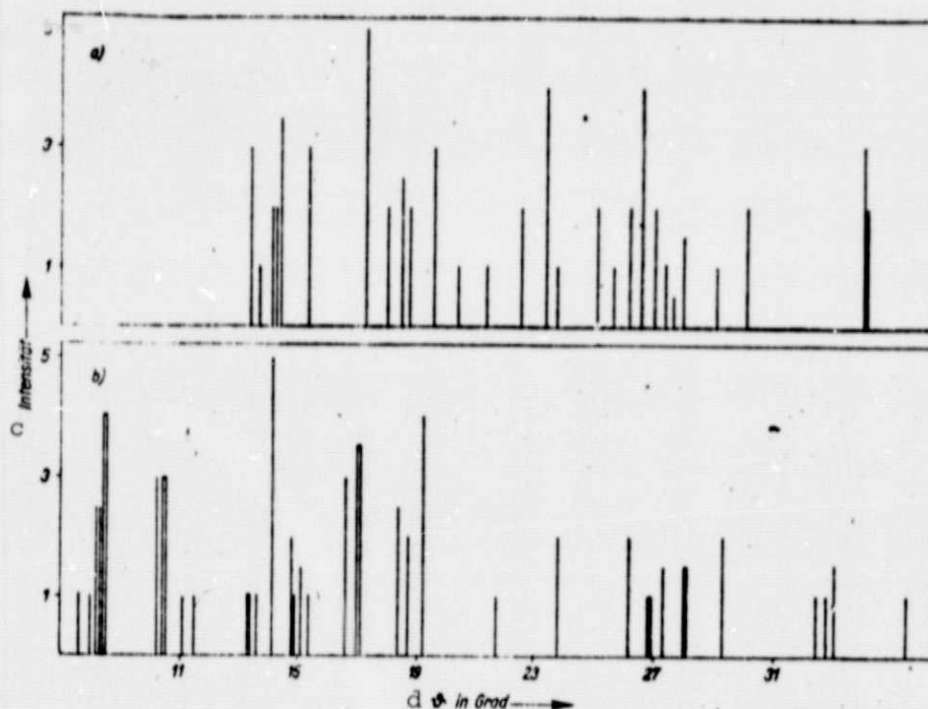


Fig. 3. X-ray interferences of: a.  $(\text{NO})\text{HSO}_4$  (after Stopperka); b.  $(\text{NO})\text{HS}_2\text{O}_7$ .  
Key: c. Intensity d.  $\theta$  in degrees

with data from other authors [5-9] for analogous substances suggests the following correlations for the characterization of this substance:

$740\text{ cm}^{-1}$ :  $\nu_{\text{S}}\text{S-O-S}$ ;  $793\text{ cm}^{-1}$ :  $\nu_{\text{as}}\text{S-O-S}$ ;  $960\text{ cm}^{-1}$ :  $\nu\text{S-OH}$ ;  $2304\text{ cm}^{-1}$ :  $\nu\text{NO}^+$ . The exact position of the absorption bands was determined by comparison with calibration spectra obtained for  $\text{NH}_3$  and  $\text{CO}$ .

X-ray diffraction readings for the same substance, given /346 in Fig. 3 together with Stopperka's data for  $(\text{NO})\text{HSO}_4$  [10], show differences in comparison with Stopperka's values; these differences, in connection with the analytical and IR-spectroscopic examinations, indicate that the substance examined, which was obtained by introducing  $\text{SO}_3$  into solutions of  $(\text{NO})\text{HSO}_4$  in anhydrous  $\text{H}_2\text{SO}_4$ , is the  $(\text{NO})\text{HS}_2\text{O}_7$  described by Wartel and Heubel [11].



Further investigations of the system are currently in progress.

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